FLAME RETARDANT INTUMESCENT POLYAMIDE 11 NANOCOMPOSITES – FURTHER STUDY

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Abstract

The objective of this research is to develop improved polyamide 11 and 12 polymers with enhanced flame retardancy, thermal, and mechanical properties for selective laser sintering (SLS) rapid manufacturing (RM). In the present study, a nanophase was introduced into the polyamide 11 and combine with a conventional intumescent flame retardant (FR) additive via twin screw extrusion. Arkema Rilsan® polyamide 11 molding polymer pellets were used with two types of nanoparticles such as: chemically modified montmorillonite (MMT) organoclays and carbon nanofibers (CNFs). Two types of Clariant's Exolit® OP 1311 and 1312 intumescent FR additives were used to generate a family of FR intumescent polyamide 11 nanocomposites with anticipated synergism.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to determine the degree of dispersion. Injection molded test specimens were fabricated for physical, thermal, mechanical properties, and flammability measurements. Thermal stability of these intumescent polyamide 11 nanocomposites was examined by TGA. Mechanical properties such as ultimate tensile strength, rupture tensile strength, and elongation at rupture were measured. Flammability properties were also obtained using the UL 94 test method. TEM and SEM micrographs, physical, mechanical, and flammability properties are presented in the paper. FR intumescent polyamide 11 nanocomposites properties are compared with polyamide 11 baseline polymers. Based on flammability and mechanical material performance, selective polymers including polyamide 11 nanocomposites and control polyamide 11 will be cryogenically ground into fine powders for SLS RM processing. SLS specimens will be fabricated for flammability, mechanical and thermal properties characterization.

1. Introduction

Polymeric resins are versatile materials and are used in a multitude of diverse areas from film, fabric to molded components for mechanical parts. Inorganic fillers such as glass fibers, mineral fillers, and metallic fillers can be incorporated into these materials to further enhance their physical and mechanical properties such as toughness, stiffness, tensile strength, chemical resistivity, etc. Although physical and mechanical properties are enhanced by fillers, these resulting materials are lacking in flame retardancy and are of limited use in consumer products

that require flame retardancy. Reduced flammability of these materials can be achieved by incorporating conventional fire retardant additives into these polymers.

Flame retardant (FR) additives such as inorganic metal oxides/hydroxides or halogens with or without phosphorous and nitrogen containing materials are required in conventional methods to modify flammable thermoplastic materials as FR products [1]. Large amounts of FR additives (>30%) are necessary when those methods are used to make FR thermoplastics. In many cases a reduction of mechanical properties, such as toughness, melt flow, and/or release of smoke and toxic emissions, occurs when the modified thermoplastic is burning.

The incorporation of nanoparticles has been shown to be an effective method for developing FR thermoplastic polymer by twin-screw extrusion (a melt blending process). It has been demonstrated that small amounts of nanoparticles (<7%) are required to make nanocomposites to exhibit similar enhanced flame retardant properties when compared with the FR thermoplastic generated by conventional methods [2-13]. However, unlike the conventional FR thermoplastics, the resulting nanocomposites exhibit enhanced mechanical properties such as high strength/modulus, moisture resistance, higher heat deflection temperature, etc. Therefore, nanotechnology can be used to develop novel FR thermoplastic structural components with high performance characteristics.

Our previous studies [14-15] indicated that low amounts (≤5%) of nanoparticles enhance the mechanical properties (such as tensile strength, flexural strength, and Young's modulus) but are somewhat lacking in flame retardancy to those FR thermoplastics with conventional FR additives. Large amounts of nanoparticles (>7%) would yield relatively good enhancement of flame retardancy, but the mechanical properties of the resulting polymer nanocomposites would be compromised. Therefore, the preparation of a truly fire retardant PA11, requires the combination of the conventional FR additives and nanoparticles together into the polymer resin. It is expected that if synergy between the FR additives and nanoparticles occurs within the PA11 resin, then the flammability and thermal properties of the resulting PA11 FR nanocomposites would be improved as compared with PA11 nanocomposite or PA11 solely with FR additives. Our related study that involved PA11 FR nanocomposites [16] demonstrated that synergism existed between the Clariant's OP1230 FR additives and Southern Clay Products' Cloisite 30B clay/Applied Science's Pyrograf® PR-19-PS CNF and superior thermal and flammability properties were observed as anticipated. Furthermore, the mechanical properties (except low tensile elongation at rupture) of these PA11 FR nanocomposites were improved when compared to those of the PA11 with only the FR additives. However, PA11 FR nanocomposites were still deficient to those of the neat PA11 or the PA11 nanocomposites [17].

Thus the major technical objective of this research program is to further enhance the mechanical properties of these PA11 FR nanocomposites by using additional, selective FR additives while maintaining the same amount of nanoclay and CNF. It is anticipated if synergism occurs between the nanoparticles and the conventional FR additives in the PA11 resin, a reduced amount of FR additives will be needed to prepare the new formulations to pass the flammability test with enhanced mechanical properties. Various weight loadings of nanoclay (5 to 7.5%), carbon nanofiber (5 to 7.5%), and the newly selected intumescent FR (15 to 25%) were melt-blended with polyamide 11 via twin-screw extrusion. The resulting pellets were injection molded into different test specimens.

Transmission electron microscopy (TEM) was used to examine the degree of dispersion of nanoparticles. Initial flammability properties were studied by conducting the UL 94 test. Thermal properties of the samples were analyzed using thermogravimetric analysis (TGA). Mechanical properties were measured in accordance with the ASTM D638. Results were compared with those of FR PA11 nanocomposites with OP1230 that were reported previously [16-17].

2. Experimental

2.1 Materials

Polymer Resin Polyamides (PA) are versatile engineering thermoplastics noted for outstanding properties such as high tensile strength, good resistance to flow under pressure (creep), excellent abrasion, chemical and heat resistance, and a low coefficient of friction. Polyamides such as PA6 and PA66 are high melting, moderately crystalline polymers (T_m 220-265°C) while PA11 and PA12 are intermediate melting materials (<200°C) and are less susceptible to moisture as compared to PA6 and PA66. Paul et al. [18] have examined the structure and properties of nanocomposites based on PA6, PA11, and PA12. Their studies were focused solely on nanoclays whereas our studies are directed to examining/comparing nanoclay and other nanoparticles to determine enhanced polymer characteristics such as flame retardancy and improved thermal/mechanical properties for the resulting PA11N.

Arkema's RILSAN® polyamide 11 (PA11) was selected for this study since it is an attractive polyamide used in a variety of applications. RILSAN® PA11 thermoplastic [19] is a polymer developed by Atofina Chemicals, Inc. (now known as Arkema, Inc.) in 1942. Derived from a series of complex chemical operations, RILSAN® PA11 is one of the few polymers that is produced from 'green' raw materials – castor beans. RILSAN® PA11 resin has earned a preferred material status in the most demanding applications due largely to their unique combination of thermal, physical, chemical, and mechanical properties. This results in an outstanding "cost performance ratio." Processing ease is another major benefit of RILSAN® polyamide 11 resins. Supplied in powder or pellet form RILSAN® PA11 resin can be processed by injection molding, extrusion, blown film extrusion, extrusion blow molding or rotomolding. The ease of processing of Rilsan® has led designers to select them for industries as diverse as aerospace, offshore drilling, electrical cables, automotive, and pneumatic and hydraulic hose.

Nanoparticles Two types of nanoparticles, nanoclay and carbon nanofiber, were used. Southern Clay Products' montmorillonite (MMT) nanoclay, Cloisite® 30B (a natural MT modified with an organic modifier, MT_2EtOT: methyl-tallow-bis-2-hydroxyethylquaternary ammonium at 90 meq/100g) was selected [20]. Achieving exfoliation of organomontmorillonite in various continuous phases is a function of the surface treatment of the MMT clays and the mixing efficiency of the dispersing equipment. Surface treatment of MMT is conveniently accomplished with the exchange of inorganic counterions, e.g., sodium etc., with quaternary ammonium ions. The second type of nanoparticles used was Pyrograf®-III PR-19-PS carbon nanofiber (CNF) from Applied Science, Inc. CNF is a form of vapor-grown carbon fiber, which is a discontinuous graphitic filament produced in the gas phase from the pyrolysis of hydrocarbons [21-24]. In regard to properties of physical size, performance improvement, and product cost, CNF complete a continuum bounded by carbon black, fullerenes, and single-wall to multi-wall carbon nanotubes on one end and continuous carbon fiber on the other end [24].

Fire Retardant Additive Clariant's Exolit® OP1311 and OP1312, which are formulated for polyamide materials, are non-halogentaed intumescent flame retardant additives based on organic phosphinate type materials. They are non-toxic, hydrophobic, and exhibit good thermal stability. Exolit materials were mixed with polyamide 66, and the resulting products showed enhanced FR properties [25-27].

2.2 Measurements

Morphological Microstructures Analysis The uniformity of the PA11 FR nanocomposites was investigated by TEM to examine the dispersion of nanoclay, carbon nanofibers, and intumescent FR additives within the PA11 polymer matrix. Uniform distribution of the nanoparticles/FR additives within the polymer matrix is essential to yield the best enhancement of material properties of the polymer matrix.

Mechanical Testing In order to compare the mechanical properties of nanocomposites, stress-strain behavior was performed using an automated tensile testing system (Instron model 3345) in accordance with ASTM D638. Ultimate tensile strength, rupture tensile strength, tensile modulus, and tensile elongation at rupture were obtained from the stress-strain data.

Thermal Stability Testing Thermal stability of the PA11 baseline and PA11N were examined by thermogravimetric analysis (TGA) using the Perkin Elmer TGA 7. Weight changes in sample materials are measured as a function of temperature or time in TGA. The sample is heated by a furnace with nitrogen while the loss or gain of sample weight is monitored by a sensitive balance. Weight, temperature, and furnace calibrations were carried out within the range of the TGA (100-900°C) at scan rates of 10°C/min and 20°C/min.

Flammability Testing UL 94, a standard test for flammability of plastic materials in industry that serves as a preliminary indication of plastics acceptability for use as a component within a device or appliance with respect to its flammability behavior. UL 94 is not intended to reflect the hazards of a material under actual fire conditions but is considered as a preliminary step toward obtaining plastic recognition and subsequent listing in the "Plastics Recognized Component Directory" (formerly known as "Yellow Cards"). The materials are tested in a vertical setting to determine the UL94 V-0 rating. UL 94 Vertical burning test involves a 1/2" x 5" specimen which is held at one end in the vertical position. A burner flame is applied to the free end of the specimen for two 10 second intervals separated by the time it takes for flaming combustion to cease after the first application. Five specimens are tested for each formulation.

3. Results and Discussion

3.1 Processing and Characterization of the Polymer Nanocomposites

Blending Nanoclays/FR Additive/PA11 Polymer Chemically treated pillared clay Cloisite® 30B and intumescent fire retardant additive Exolit® OP1311 and 1312 were used. The individual clay layers are separated by alkyl ammonium ion incorporation (d spacing increased) allowing for anticipated intercalation of solid organic resins when the clay is melt blended with the resins. Clays were blended with the PA11 resin to intercalate and eventually exfoliate the clay. Twin screw extrusion mixing enhances the exfoliation rate. The degree of exfoliation is examined by TEM.

A 30 mm Werner Pfleider corotating twin screw extruder which is configured for a wide

variety of materials was used. The extruder L/D can be varied from 21 to 48, with options of multiple feeds and vents. The energy profile of the screw is adjusted to optimally meet the needs of the target product. Table 1 shows the nanoparticles and FR additives selected at various wt% loading levels with the PA11 resin. For the clay a relatively long residence time is preferred for the screw profile allowing high shear characteristics for complete separation of the nanoclay platelets so that the polymer matrix is dispersed uniformly into the clay galleries. Approximately 10 lbs of each formulation were produced. Separate volumetric feeders were used for the base resin and the nanoparticles. The PA11 was dried in a desiccant drier before compounding. Injection molded specimens of each blend were prepared and examined by TEM.

Figure 1 shows the TEM micrographs of polyamide 11 with 15% OP1311 and 5% Cloisite® 30B. It is evident that exfoliation of Cloisite® 30B in PA11 polymer was achieved. The micro-sized FR intumescent FR additives were also uniformly dispersed in the PA11 polymer.

Table 1 Composition of various formulations of FR PA11N and UL 94 results

Formulations			UL 94	Formulations			UL 94
#	FR	NP	Rating	#	FR	NP	Rating
1	PA11 neat		Failed	20	30% OP1230		V-0
2	15% OP1311	5% 30B	Failed	6	15% OP1311	5% CNF	V-1
3	15% OP1311	7.5% 30B	V-1	7	15% OP1311	7.5% CNF	V-1
4	20% OP1311	5% 30B	V-1	8	20% OP1311	5% CNF	V-0
5	20% OP1311	7.5% 30B	V-0	9	20% OP1311	7.5% CNF	
10	10% OP1312	5% 30B	Failed	16	15% OP1312	5% CNF	V-1
11	15% OP1312	5% 30B	Failed	17	15% OP1312	7.5% CNF	V-1
12	15% OP1312	7.5% 30B	V-1	18	20% OP1312	5% CNF	V-0
13	20% OP1312	5% 30B	V-0	19	20% OP1312	7.5% CNF	V-0
14	20% OP1312	7.5% 30B	V-0				
15	25% OP1312	5% 30B	V-0				
21	20% OP1230	5% 30B	V-1	24	20% OP1230	5% CNF	V-0
22	20% OP1230	7.5% 30B	V-0	25	20% OP1230	7.5% CNF	V-0
23	25% OP1230	5% 30B	V-1	26	25% OP1230	5% CNF	V-0

Blending CNF/FR Additive/PA11 Polymer PR-19-PS CNF possesses a diameter of about 130 nm and a length of several microns. It can be classified as MWNT. It was blended with PA11 polymer along with FR additive in three different loading levels via twin screw extrusion (Table 1). For the CNF, the screw was configured to allow separation of the CNF without fracturing them. Figure 2 shows the TEM micrographs of polyamide 11 with 15% OP1311 and 5% CNF. The CNF was also well dispersed in the matrix.

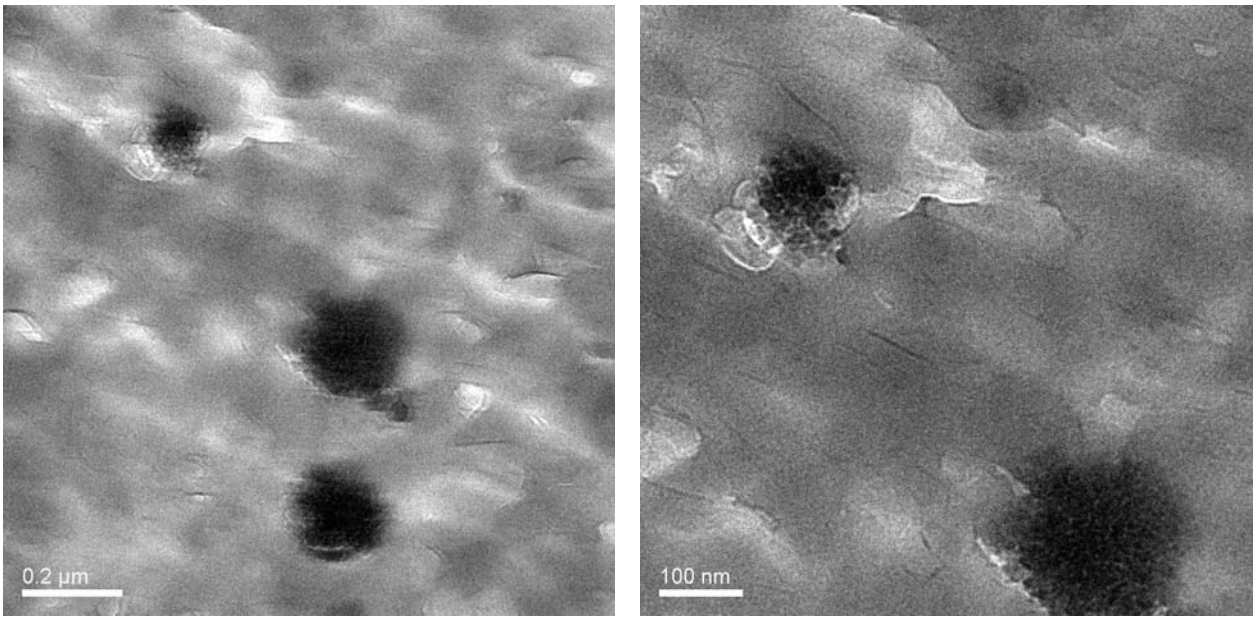

Figure 1 TEM micrographs of polyamide 11 with 15% OP1311 (large dark micron-sized particles) and 5% Cloisite® 30B (hairline 1 nm thick platelets) polymer showing exfoliation of nanoclay in PA11 was achieved.

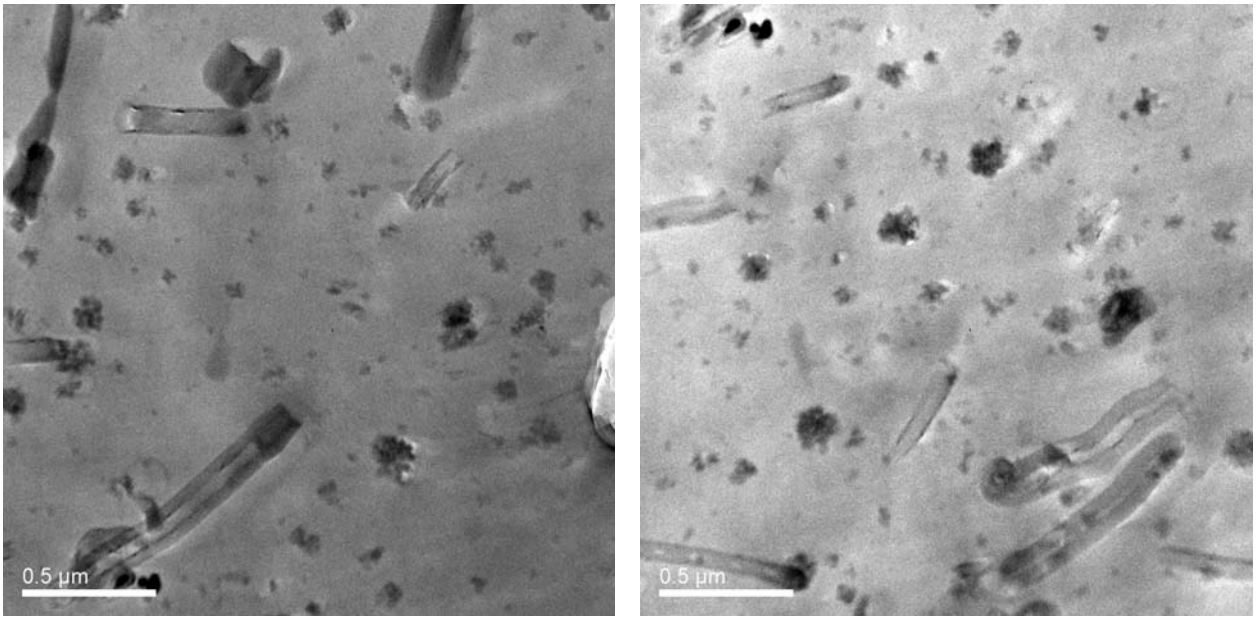

Figure 2 TEM micrographs of polyamide 11 with 15% OP1311 (dark micron-sized particles) and 5% PR-19-PS CNF (elongated fibers).

3.2 Mechanical Properties of the Polymer Nanocomposites

Ultimate tensile strength, rupture tensile strength, tensile modulus, and tensile elongation at rupture of the PA11 FR nanocomposites were measured (Figures 3-6). In all cases beside tensile modulus, the PA11 FR nanocomposites with 5%CNF had better properties than those with

5%30B possessing the same type and loading level of FR additives. At a constant amount of 30B and combined with OP1312, that composition yielded the best ultimate tensile strength and rupture tensile strength, while for CNF, OP1230 gave the best results.

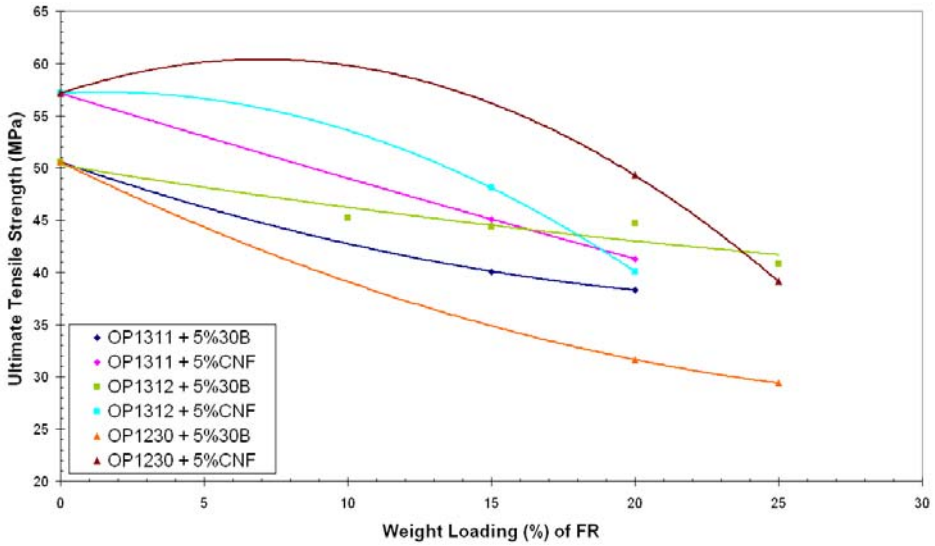

Figure 3 Ultimate tensile strength of PA11 FR nanocomposites with 5% nanoparticles.

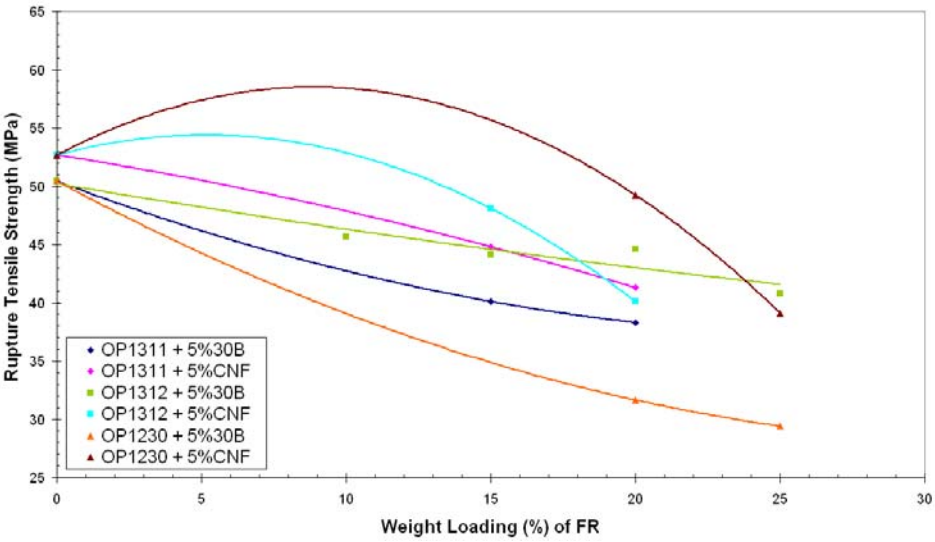

Figure 4 Rupture tensile strength of PA11 FR nanocomposites with 5% nanoparticles.

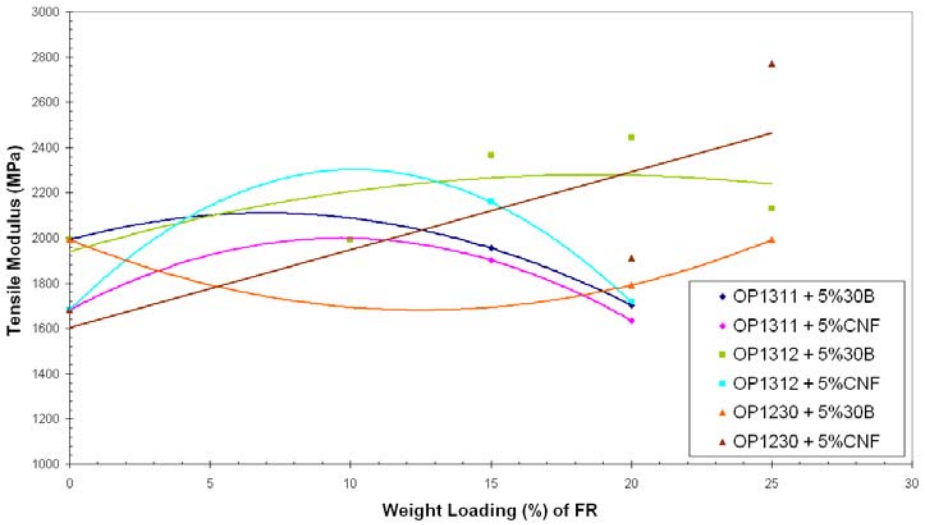

Figure 5 Tensile modulus of PA11 FR nanocomposites with 5% nanoparticles.

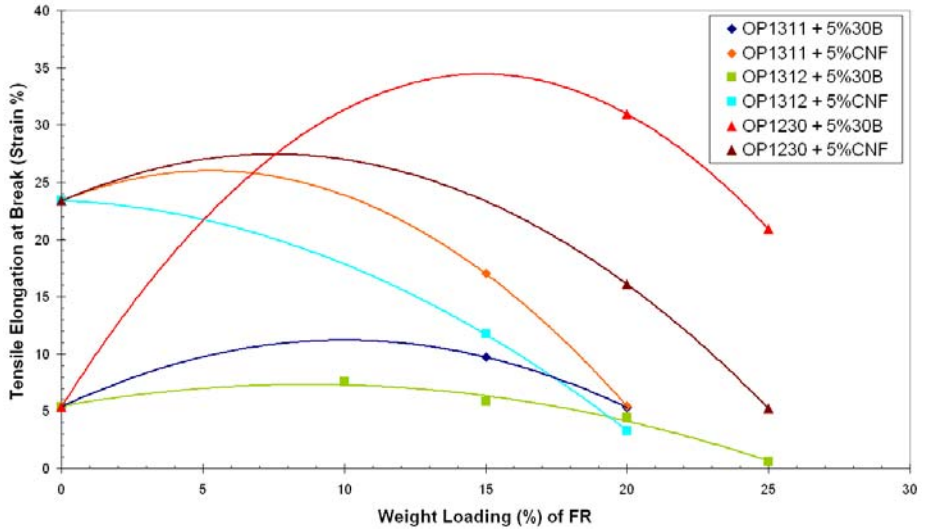

Figure 6 Tensile elongation at rupture of PA11 FR nanocomposites with 5% nanoparticles.

3.3 Thermal Stability of the Polymer Nanocomposites

TGA was performed on all formulations under nitrogen using the heating rate of 20°C/min (Figures 7-9). In all cases, PA11 FR nanocomposites had better thermal stability or higher decomposition temperatures than the neat PA11 or the related solely PA11 nanocomposites. Furthermore, PA11 FR nanocomposites with 5% 30B had better thermal stability than those with 5% CNF and same type and loading level of FR additives. At the loading of 5% 30B and combined with OP1230, the resulting composition exhibited the best thermal stability, while for CNF combined with OP1230, it possessed the highest decomposition temperature at 10% mass loss but OP1312 provided the highest decomposition temperature at 50% mass loss.

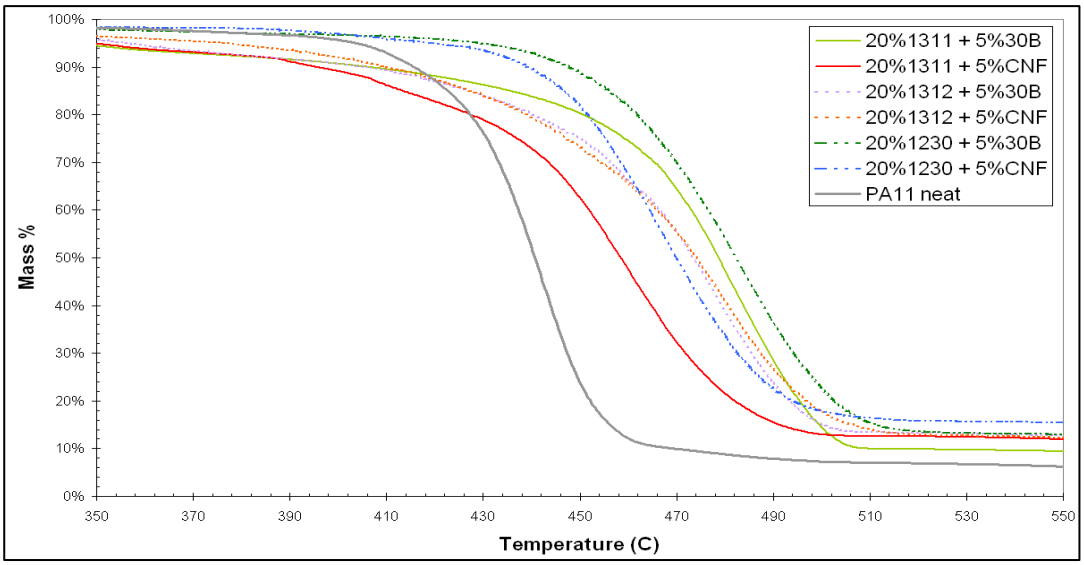

Figure 7 Thermogravimetric analysis of PA11 FR nanocomposites with 20% FR and 5% nanoparticles at 20°C/min in nitrogen.

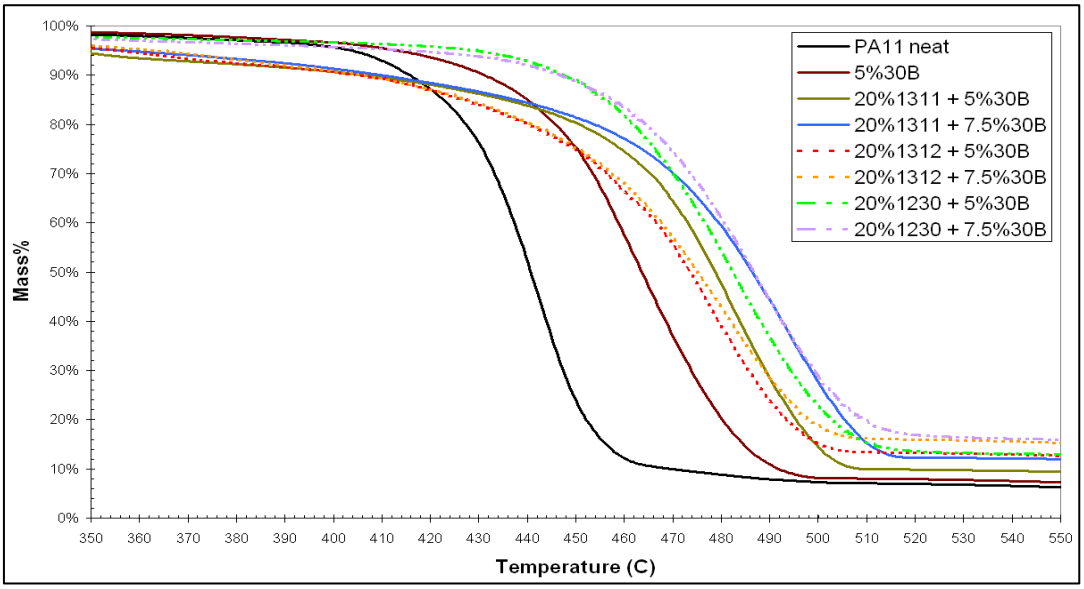

Figure 8 Thermogravimetric analysis of PA11 FR nanocomposites with 20% FR and Cloisite 30B at 20°C/min in nitrogen.

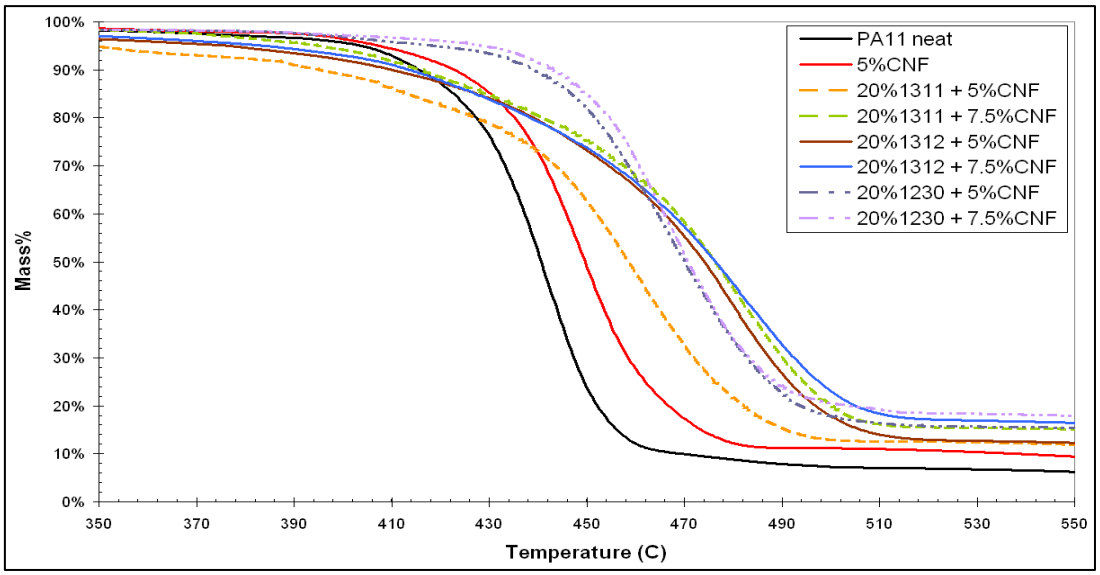

Figure 9 Thermogravimetric analysis of PA11 FR nanocomposites with 20% FR and CNF at 20°C/min in nitrogen.

3.4 Flammability Properties of the Polymer Nanocomposites

The materials were tested as "received with no additional conditioning/drying" for UL 94 testing. The test was performed in our lab and the UL 94 testing requirements. Procedures were followed as stringently as possible. Our lab is not certified for UL 94, and the results serve as a screening tool. Five specimens were tested for each formulation (except formulation #9 in Table 1 since specimens were not available). The testing was performed in a fume hood with a preset airflow of 90-105 ft/min. Fume hood sash was pulled down as much as possible to prevent airflow from the outside environment. The erratic exhaust airflow from the fume hood and the surrounding made the reproducibility of the testing challenging. The burner is lit during the time of this experiment to keep the applied flame constant between each specimen. Table 1 shows the UL 94 results. It showed that even though the FR additives were used together with nanoparticles, loadings of 10% and 15% of FR additives were insufficient for V0 rating. Moreover, of all the formulations with 5% 30B and 20% FR additives (#4, 13, and 21), only 30B combined with OP1312 achieved the UL94 V0 rating. In regard to CNF, all formulations with at least 20% FR additives and at least 5% CNF achieved UL94 V0 rating. It seems that CNF exhibited a better synergistic effect with all three types of FR additives than 30B as it related to flammability retardancy.

4. Summary and Conclusions

A total of 26 polymer blends of polyamide 11 polymer with MMT nanoclay/carbon nanofiber and intumescent fire retardant additive were compounded separately via twin screw extrusion. Injection molded specimens of PA11 baseline and FR-PA11N were fabricated for physical, mechanical, thermal, and flammability properties measurements. Some results were also compared with PA11 clay nanocomposites. Transmission electron microscopy was used to examine the dispersion uniformity of the nanoparticles in the polyamide 11 resin. Thermal

stability of PA11N was analyzed using thermogravimetric analysis. Flammability properties were measured by UL 94 test.

The following conclusions were drawn from this study:

1. The TEM analysis has shown that good dispersions of either nanoclays or carbon nanofibers in the polyamide 11 resin systems were achieved.
2. In regard to mechanical properties, OP1312 exhibited enhanced flame retardance with 30B while OP1230 performed better with CNF.
3. In terms of thermal stability, OP1230 was best when combined with 30B while OP1312 was best with CNF.
4. As it related to flammability properties, 30B combined best with OP1312 while CNF performed well with all three FR additives.
5. In this study, a minimum of 20% FR additives is needed to pass the UL 94 V0 rating.
6. The threshold amount of FR additives needed to achieve UL94 V0 rating can be lower (between 15% and 20%) but needs further investigation.
7. A third element, e.g. elastomer, may be required to further improve toughness.
8. Selected formulations will be chosen for SLS fabrication.

5. References

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